Partial Oxidation of CH_4 to HCHO over a MoO_3-SiO_2 Catalyst: A Kinetic Study

There is considerable economic incentive to convert methane into formaldehyde, which is used in the manufacture of insulating materials and adhesives. This paper discusses the kinetics of a one-step oxidation of methane with molecular oxygen over a MoO_3-SiO_2 catalyst. The space velocity was varied between 2,500 and 10,000 h^{-1} (at NTP) over a range of temperatures from 848 to 923 K.

Selectivities to formaldehyde between 30 and 89% were observed in the 0–5% methane conversion range, the other principal products being CO, CO_2, and H_2O. Kinetic analysis indicates that methane is directly oxidized to CO_2 and HCHO, with HCHO being further oxidized to CO. The reactions were all found to be zero order in oxygen concentration, with methane and formaldehyde oxidation following overall first-order rate laws. Kinetic rate constants have been determined and there is good agreement between model predictions and experimental data.

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Introduction

Methane accounts for over 60 vol. % of natural gas, which is primarily used as a fuel. Methane is also found in refinery effluent gas streams, at oil wells, and in remote geographic areas. At these locations, methane is often flared, since the fuel value cannot easily be redeemed. Due to its great abundance and low cost, on a carbon basis, there is a strong economic incentive to turn methane into other value-added products. This is presently done by steam reforming methane to syngas, converting syngas to methanol, and then by transforming methanol into chemicals. For example, methanol may be oxidized to formaldehyde, a raw material in the manufacture of insulating materials and adhesives, using a commercially available catalytic process. Recently developed technologies using shape-selective zeolite catalysts may also be used to convert methanol to chemicals such as ethylene and propylene (Kaeding and Butter, 1980), or into liquid fuels (Meisel et al., 1976).

Steam reforming of methane to syngas is an endothermic process, requiring very high reactor temperatures. Methanol synthesis and the subsequent conversion processes are exothermic and heat removal is a problem. Clearly, a one-step process for the oxidation of methane to chemicals would be an appealing

alternative to the presently practiced routes, with great potential savings in capital expenses and reduced operating costs because of the lower energy consumption.

The thermodynamically favored products of hydrocarbon oxidation are carbon oxides and water. However, several important industrial processes are based on the catalytic partial oxidation of aliphatic hydrocarbons. Among these are the epoxidation of ethylene (Sachtler et al., 1981) and the ammoxidation of propylene (Grasselli, 1986).

As is shown in Figure 1, the reaction of methane and oxygen produces very small amounts of methanol and formaldehyde at equilibrium. Methane has, however, been oxidized to other products using catalysts. Although there are numerous patents on the catalytic partial oxidation of methane (Imre, 1975, 1976; Dowden and Walker, 1968; Stroud, 1971), only relatively few papers have been written on this subject. Recent work (Khan and Somorjai, 1985; Liu et al, 1984; Iwamoto 1983a,b) has concentrated on the oxidation of methane by N_2O in the presence of water. The major oxidation products have been methanol, formaldehyde, carbon monoxide, and carbon dioxide.

In the present work, molecular oxygen has been used for the partial oxidation of methane over a molybdena-silica catalyst (Spencer, 1986). Formaldehyde, carbon monoxide, carbon dioxide, and water were found to be the primary oxidation products. A kinetic model that describes the conversion and selectivity for methane oxidation is proposed.
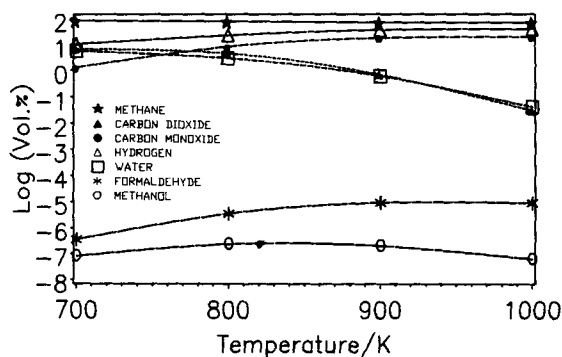
Figure 1. Equilibrium concentrations after reaction at 1 atm.

Initial gas mixture: methane 90 vol. %, oxygen 10 vol. %

Experimental Procedures

Catalyst preparation

The silica support used was either fumed (Cabosil M5), or a silica gel (Davison ID) which had been washed in a stream of dilute sulfuric acid (pH = 3) for several days at 373 K in order to reduce the sodium level to below 10 ppm. The fumed silica was impregnated with an ammonium paramolybdate solution by incipient wetness. In the case of the gel, the components were simply slurried together and the mixture evaporated to dryness. After impregnation, the catalysts were dried at 483 K and then calcined for 2–3 h at 873 K. The final catalyst contained 1.8 wt % Mo on a total catalyst basis. Prior to testing, the catalysts made from fumed silica were compressed and crushed, and all catalysts were screened to a particle size of 0.5–0.7 mm. The BET surface areas of the catalysts were 195 $m^2 \cdot g^{-1}$ for the MoO_3-fumed silica and 277 $m^2 \cdot g^{-1}$ for the MoO_3-silica gel.

Catalyst testing

The test reactor consisted of a 0.95 cm OD quartz tube containing a quartz frit. 0.2 g of catalyst was placed on the frit, and covered with an equal volume of fused quartz chips (General Electric Co.) that had been crushed and screened to 0.5–0.7 cm diameter. This quartz layer served as a preheating zone. A stainless-steel clad type K thermocouple was placed at the junction of the quartz and the catalyst and the reactor placed on the axis of a radiant heating chamber (Research Inc.). The outside of the
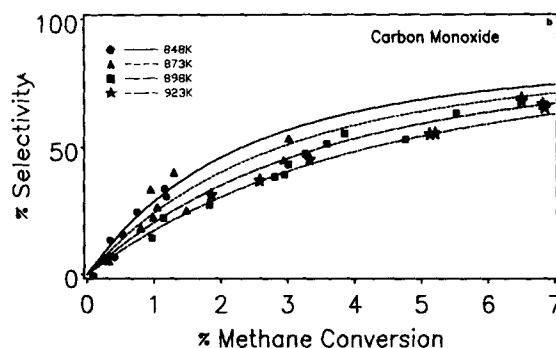

Figure 2b. Selectivity vs. methane conversion for carbon monoxide.

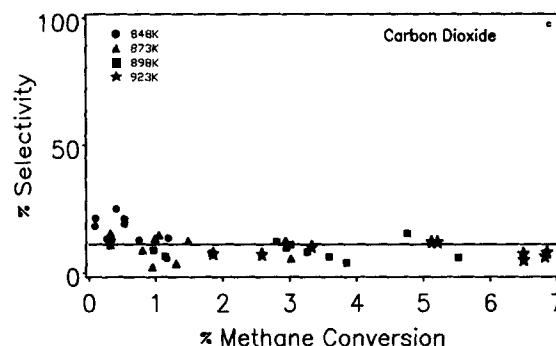Points: exp. data; curves: model calculations

Figure 2c. Selectivity vs. methane conversion for carbon dioxide.

Points: exp. data; curves: model calculations

quartz reactor was painted with platinum black in order to maximize absorbance of the radiation and eliminate radiation-induced artifacts. Methane and oxygen (MG purity, MG Inc.) were passed through mass flow controllers and mixed prior to their entry into the quartz reactor. All reactions were carried out at 1 atm. The methane to oxygen molar ratio was varied between 9:1 and 25:1 over a range of space velocities from 2,500 to 10,000 h^{-1} (GHSV, gas hourly space velocity at NTP) and temperatures of 848, 873, 898, and 923 K.

The reactor effluent was led through heat-traced lines (373 K) to a gas chromatograph (Shimadzu, Inc.) with argon
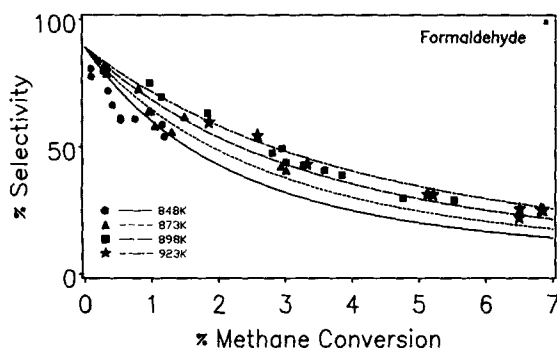

Figure 2a. Selectivity vs. methane conversion for formaldehyde.

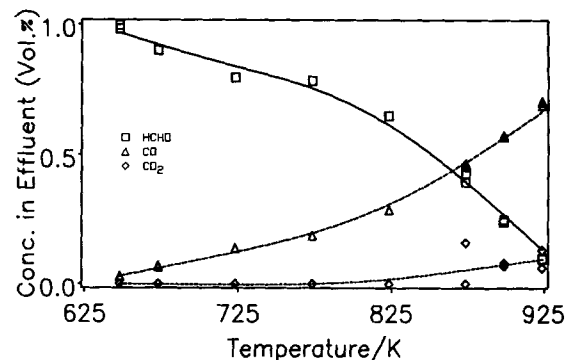Points: exp. data; curves: model calculations

Figure 3. Product gas distribution during oxidation of HCHO entrained in argon: oxygen mixture.
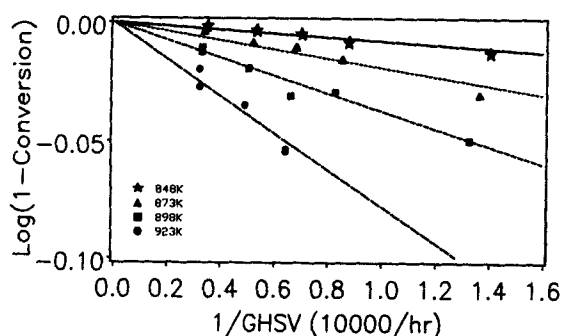
MoO_3-silica gel catalyst

Figure 4. Rate constant plot based on Eq. 1 for MoO₃-silica gel catalyst.

A similar plot was obtained for fumed silica-based catalyst

Figure 6. Arrhenius plot for k_1 and k_3.

Plot based on data graphically derived from Figures 4 and 5

carrier gas, where O_2, CO, CO_2, and CH_4 were analyzed with a Carbosphere column and a thermal conductivity detector. Formaldehyde was analyzed using a Porapak T column and either a thermal conductivity detector, a photoionization detector (11.7 eV lamp), or a flame ionization detector preceded by a methanator. Similar results were obtained using all three techniques, and they were all independently calibrated against the wet chemical chromatropic acid method (West and Sen, 1956).

The formaldehyde source in the HCHO oxidation experiments consisted of paraformaldehyde powder in a washbottle that was thermostatted at about 350 K. A mixture of argon and oxygen was passed through mass flow controllers into the paraformaldehyde bottle, and thence through heat-traced lines into the reactor. Analytical methods were as described above.

Results

The primary products of methane oxidation were found to be formaldehyde, carbon dioxide, carbon monoxide, and water. Methanol and hydrogen were only present in trace quantities. Reactor effluent data obtained under varying operating conditions are displayed in the form of product selectivity (the percentage of product in the converted methane) vs. percent methane conversion. As shown in Figure 2a, the formaldehyde selectivity decreases monotonically with methane conversion. Formaldehyde selectivity of 89% is observed at the limit of zero methane conversion, indicating that HCHO is a primary reaction product. At a given level of methane conversion, formaldehyde selectivity increases with increasing temperature. Selectiv-
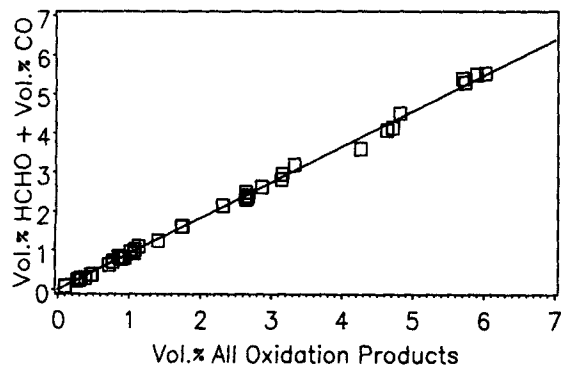
ity to carbon monoxide is zero at zero methane conversion and increases with methane conversion, implying that carbon monoxide is a secondary product, Figure 2b. At a fixed methane conversion, carbon monoxide selectivity decreases with increasing temperature. Selectivity to carbon dioxide is fairly constant and carbon dioxide is a primary product, with a selectivity around 11% at zero methane conversion, Figure 2c. No change in conversion or selectivity behavior was detected when the $CH_4:O_2$ molar ratio was varied between 19:1 and 6:1, providing that oxygen conversion was kept below 100%. This strongly suggests that the reaction is zero order in oxygen, as is the case with several other hydrocarbon partial oxidation reactions (Monnier and Keulks, 1979; Grasselli and Suresh, 1972). Virtually identical curves were obtained over the fumed silica and the silica-gel supported catalysts.

In order to probe the further oxidation of HCHO independently, formaldehyde gas was entrained in 9:1 argon:oxygen at a level of 1.2 vol. % and the mixture passed over the same catalyst bed as had been used for the methane oxidation reactions. The GHSV was held at 5,000 h⁻¹ (NTP) and the temperature varied from 648 to 923 K. The effluent composition as a function of temperature is shown in Figure 3. HCHO primarily oxidizes to carbon monoxide and very little carbon dioxide is found in the reaction products.

Based on the above observations the following kinetic mechanism may be proposed:

$$CH_4 + O_2 \xrightarrow{k_1} HCHO + H_2O$$

Figure 5. $k_1/(k_1 + k_3)$ plot based on Eq. 2.

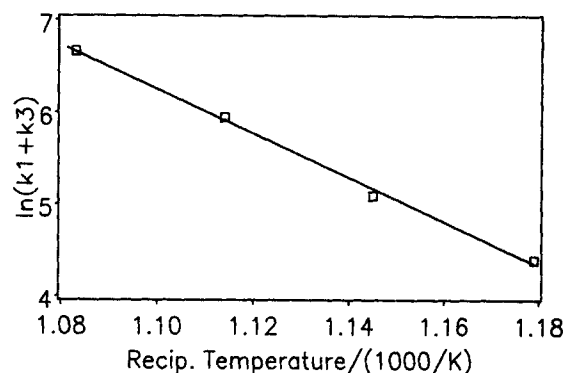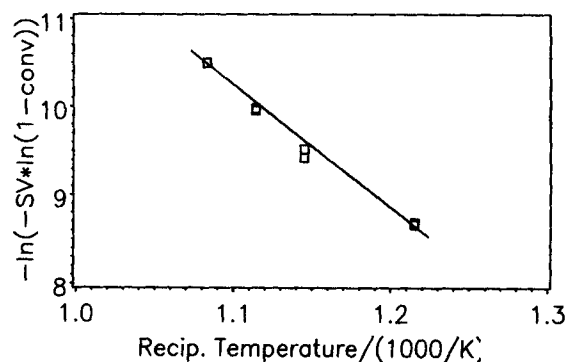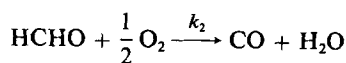Conditions as for Figure 4; data from both fumed silica- and silica gel-based catalysts
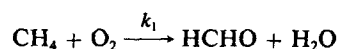
Figure 7. Arrhenius plot for k_2.

Plot based on data graphically derived from Figure 3.

$$HCHO + \frac{1}{2} O_2 \xrightarrow{k_2} CO + H_2O$$

$$CH_4 + 2O_2 \xrightarrow{k_3} CO_2 + 2H_2O$$
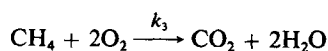
Neglecting the slight increase in the number of moles as a result of the reaction, the relationships between the various species and reactor conditions for first-order reactions in the isothermal plug flow reactor are:

$$\ln\left[1 - \frac{C_{HCHO} + C_{CO} + C_{CO_2}}{C^0_{CH_4}}\right] = -\frac{(k_1 + k_3)}{GHSV} \quad (1)$$

$$C_{HCHO} + C_{CO} = \frac{k_1}{(k_1 + k_3)}(C_{HCHO} + C_{CO} + C_{CO_2}) \quad (2)$$

where c is the mole fraction, GHSV is the gas hourly space velocity at reaction conditions, and the k's are the reactor-volume-based rate constants.

The lefthand side of Eq. 1 is plotted vs. $1/$GHSV in Figure 4. The resulting straight lines confirm that methane oxidation is indeed a first-order reaction. At each temperature, $k_1 + k_3$ is obtained from the slope of each line. The Thiele modulus was calculated at each temperature using $k_1 + k_3$ and an effective diffusion coefficient estimated from the literature (Smith, 1970). The methane oxidation reaction was found to be kinetically controlled and not limited by intraparticle diffusion. In accordance with Eq. 2, $c_{HCHO} + c_{CO}$ is plotted against $c_{HCHO} + c_{CO} + c_{CO_2}$ in Figure 5. A single straight line is obtained, confirming that formaldehyde and carbon dioxide are formed from methane via parallel reaction paths. Since the slope of the line (0.89) corresponds to $k_1 (k_1 + k_3)$ at any given temperature, the single line means that the activation energies for the formation of formaldehyde and carbon dioxide are approximately the same. An Arrhenius plot for $k_1 + k_3$ is shown in Figure 6.

The formaldehyde oxidation reaction, which was investigated independently, was found to be first order in formaldehyde concentration. The solution of the mass conservation equation in a plug flow reactor is:

$$\ln\left[-GHSV \ln\left(1 - \frac{C_{CO}}{C^0_{HCHO}}\right)\right] = \ln k^0_2 - \frac{E_2}{RT} \quad (3)$$

The lefthand side of Eq. 3 is plotted vs. $1/T$ in Figure 7 and k_2 and E_2 are obtained. A summary of the rate constants and activation energies is given in Table 1. Our value for the activation energy of k_1 (189 kJ $\cdot$ mol^{-1}) is quite close to the 168 $\pm$ 8 kJ $\cdot$ mol^{-1} determined by Khan and Somorjai (1985) for the oxida-
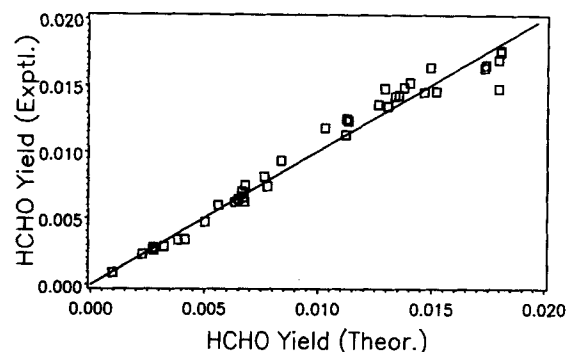

Figure 8. Comparison of experimental and model-calculated formaldehyde yield.

tion of methane to formaldehyde at comparable temperatures using N_2O as an oxidant.

The model is used to predict formaldehyde yield and, as shown in Figure 8, predictions are in good agreement with experimental data. The relationships between product selectivities and the methane conversion can be derived analytically and are summarized in Table 2. For the reaction scheme proposed, selectivities depend on the methane conversion and on temperature. The lines in Figures 2a through 2c are model predictions at each temperature. Again, model predictions follow the experimentally observed trends quite well. The maximum difference between observed and predicted formaldehyde selectivity is at the lowest temperature of 848 K and this is due to the experimental difficulties in measuring product concentrations at methane conversion levels of less than 1%.

The model is built on the assumption that the reaction rate is zero order in oxygen concentration. This assumption should break down when the oxygen concentration becomes very low. This régime was not extensively investigated, since a reduction of MoO_3 to MoO_2 was found to occur when inlet oxygen levels were reduced so much that oxygen was no longer present in the exit stream. This change in the catalyst surface chemistry was accompanied by a drastic decrease in HCHO formation in favor of the production of carbon oxides. Other reasons for selecting the range of operating conditions examined in this paper are as follows. The oxygen concentration in the methane-oxygen reactant mixture was kept low and well below the explosion limit at 923 K. As a result, the methane conversion was limited by the amount of oxygen present and in no case exceeded 7%. At temperatures above 923 K, selectivity to HCHO continued to increase, but was somewhat lower than predicted by the present

Table 1. Rate Constants and Activation Energies

Index, i	k_i at 923 K h^{-1}	E_i kJ $\cdot$ mol^{-1}
1	695	189
2	34,300	134
3	86	189

Table 2. Product Selectivity* Expressions for Methane Oxidation

$$S_{HCHO} = \frac{k_1}{(k_1 + k_3 - k_2)\psi}[\psi - 1 + (1 - \psi)^{k_2/k_1 + k_3}]$$

$$S_{CO_2} = \frac{k_3}{(k_1 + k_3)}$$

$$S_{CO} = \frac{k_1}{(k_1 + k_3)} - \frac{k_1}{(k_1 + k_3 - k_2)\psi}[\psi - 1 + (1 - \psi)^{k_2/k_1 + k_3}]$$

*Selectivity is mole fraction of total oxidized products

model. This is presumably due to the onset of other reactions, such as gas-phase HCHO oxidation, $CO \rightarrow CO_2$, and the water-gas shift reaction.

Acknowledgment

Notation

c = mole fraction, mol/total mol
E = activation energy, J/mol
GHSV = gas hourly space velocity, m³ gas/h · m³ catalyst
k = rate constant, h⁻¹
R = gas constant, J/mol · K
S = mole fraction of total oxidized products (selectivity)
ψ = mole fractional conversion of methane

Superscript

o = initial value

Subscript

i = index

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